

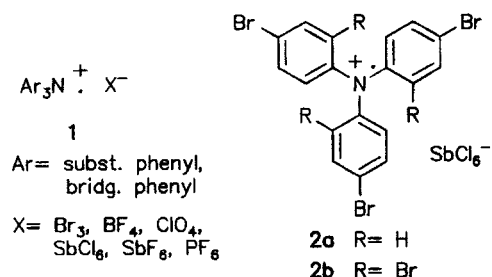
Tris(4-bromophenyl)aminium and Tris(2,4-dibromophenyl)aminium Cation Radicals – Synthetically Useful One Electron Oxidants

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Since the isolation of the first stable triarylaminium salts by Wieland, Weitz and Schwechten [1] many examples of this type of stable cation radicals (**1**) have been synthesized and characterized by spectroscopic methods as well as by electrochemical methods [2].



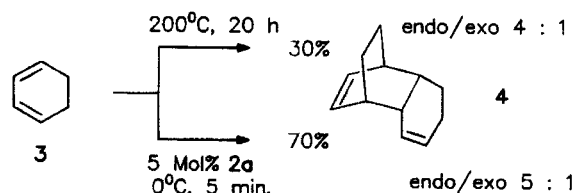
During the last three decades the cation radicals **1** and especially **2a**, **b** became useful one electron oxidants in different types of synthetically important transformations. The advantages of the oxidants **1** are:

- (1) they are stable for months when stored under nitrogen atmosphere;
- (2) they are easily prepared from the corresponding amines by oxidation with NOBF_4 or SbCl_5 ;
- (3) the only by-product in electron transfer reactions is the starting amine, which may be recovered and reoxidized;
- (4) reactions proceed under very mild conditions. Additionally, the oxidation potential can be varied over a wide range by changing the substituents within the aromatic rings, therefore the suitable oxidant for special applications may be selected.

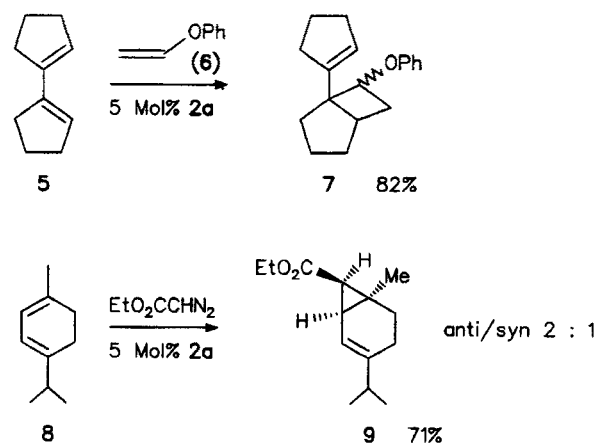
In most cases the title compound **2a** ($E = 1.3 \text{ V vs NHE}$) is used because of its easy preparation and commercial availability (Aldrich, Janssen). **2a** can be used as the stable salt or generated *in situ* in an electrochemical process [3]. If the oxidation potential of the substrate is too high, **2a** may be replaced by **2b** ($E = 1.74 \text{ V vs NHE}$). The following examples illustrate the potential of **2a**, **b** for synthetic purposes. Depending on the type of reaction **2a**, **b** are used either in catalytic or equimolar amounts.

Compounds **2a**, **b** are effective catalysts for different cycloaddition reactions proceeding via cation radical chain pro-

cesses [4]. For example the Diels-Alder dimerization of the low reactive diene **3**, which normally requires high temperature and long reaction time to give an optimum yield of 30% **4**, is catalyzed by **2a** in an impressive manner at low temperature, characterized by short reaction time, higher yield and higher *endo*-selectivity [5].

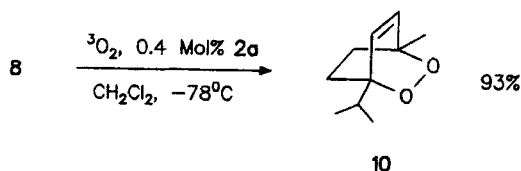


The same catalytic efficiency of **2a** is shown in the cyclobutanation of **5** and in the cyclopropanation of **8** leading to **7** and **9**, respectively, with high yields [6].

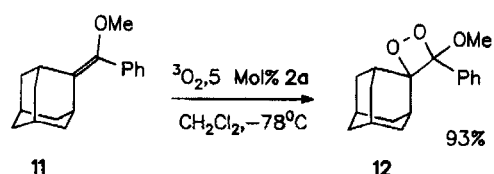


The cycloaddition of triplet oxygen to dienes, a spin forbidden reaction, is effectively catalyzed by **2a** at -78°C in the dark. The synthetic value of this reaction was demonstrated in the synthesis of endoperoxides from terpenoidal and

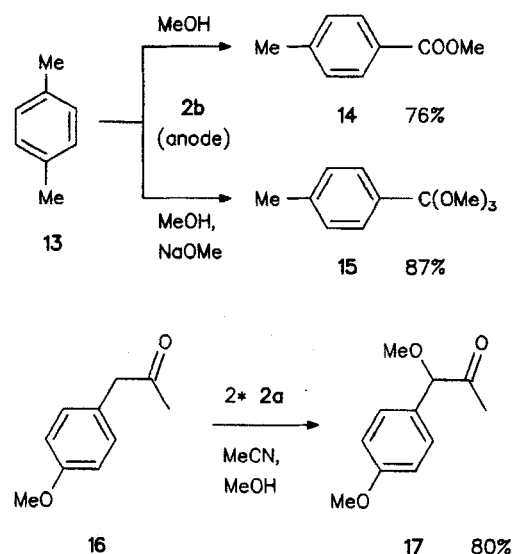
steroidal dienes [7] and is shown here in the preparation of ascaridole (**10**) from α -terpinene (**8**) with excellent yield.



Dioxetanes (e.g. **12**) which are difficult to prepare by other methods were synthesized with high yields from the corresponding olefins (**11**) using triplet oxygen and **2a** or **2b** as catalysts [8].

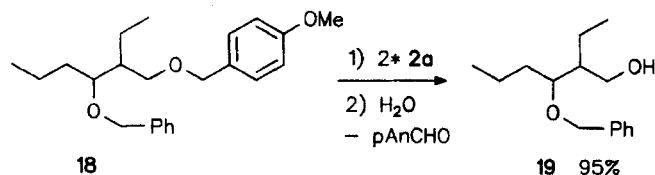


In indirect electrochemical reactions **2b** is a mild oxidant, suitable for oxygen transfer reactions for example the α -methoxylation of ethers and acetals [9]. Alkylbenzenes (e.g. **13**) are converted to esters (**14**) or orthoesters (**15**) depending on the reaction conditions using electrochemically generated **2b** [10]. Direct α -hydroxylation or α -alkoxylation of ketones with **2a** as oxidant was achieved in the presence of O-nucleophiles [11]. In this way the α -methoxy ketone **17** was prepared by the oxidation of **16** with **2a** in presence of methanol with good yield.

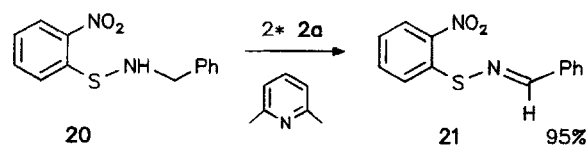


In the synthesis of natural products, i.e. proteins, sugars or terpenes, **2a** has been recognized as a convenient reagent for the mild oxidative cleavage of protecting groups as benzyl ethers, benzyl thioethers, benzyl esters, dithioacetals,

thioesters or S-glycosides [12]. For example the benzyl ether **19** was prepared in high yield by the selective deblocking of the 4-methoxybenzyl ether function of **18** employing **2a** as oxidant.



Another application of **2a** is the dehydrogenation of HN-, HO- or HS-compounds, shown here in the selective oxidation of the sulfenamide **20** [13].



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